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FIELD-EFFECT IN ELECTROCHEMICAL REACTIVITY OF ALKYLARYLSELENIDES

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Abstract—The anchimeric assistance of some substituents bearing the carbonyl group alters the nature of the potential-determining reaction of the cation radicals of alkylarylselenides,—instead of a charge-controlled fragmentation of the first order characteristic for these kinds of particles, the orbital-controlled second order disproportionation of dimerization take place.

Key words: electrooxidation, reactivity, field-effect, cation radicals, alkylarylselenides

INTRODUCTION

The electrochemical reactivity of the majority of organic selenides studied up until today in electrooxidation processes is determined by the HOMO formed by the π-electrons of an aromatic ring and by the unshared electron pair of the selenium[1–7]. When two aromatic rings are linked with Se, the cation radicals (CRs) of such compounds show the second order potential-determining reaction[8–11]; for CRs of selenides carrying only one aromatic ring, first order reactions[6, 12–14], if not a dissociative process are observed, especially for dialkylselenides.

In terms of donor-acceptor (inductive and mesomeric effects) and steric effects of substituents at the different positions of the PhSe moiety the reactivity of alkylarylselenides is unequivocally described by multiparameter correlations of E_{ox} with σ^+, σ^*, $-E_s$ and R_s type constants[6, 9], but from these models it is not clear whether the fragmentation of CRs of alkylarylselenides is the only reaction inherent to them.

Meanwhile to be able to comprehend the pathways of bulk reactions leading to the final products one has to know the identity of the primary reactions of the CRs primarily formed.

In order to reveal the factors governing the nature of the potential-determining step of the oxidation of alkylarylselenides, we have synthesised and studied a number of compounds, which, when chosen, the following were taken into account:

(i) The charge density in CR is localised preferentially on the Se atom†.

(ii) The alteration of the control of the potential-determining reaction (charge-controlled vs. orbital-controlled 2nd order interactions) could be achieved by lowering the hardness of the reaction centre or, in other words, by lowering the charge density localisation on Se.

The latter can be effected by introducing into the alkylarylselenides molecules the appropriate substituents which are able to affect the reaction centre by donor I and M-effects or by the anchimeric donor assistance.

EXPERIMENTAL

Instrumentation

Voltammetric measurements were carried out using the PU-I polarograph, which was coupled with a microcomputer BK-0010 equipped with the home-made acquisition card based on 1113-PV1A analogous-digital converter. Rotation sweep of the electrode was controlled by the FP-37 numeric counter. A Pt oxidised *rde* in the three electrode

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† This proved by dipole moments of alkylarylselenides, by ionisation potentials PI of comprising groups and by the NMR chemical shifts[3, 4, 11, 15–17]; The $E_{1/2}$ of oxidation being close for many arylselenides[5–14]; the correlation of $E_{1/2}$ as well as $h\nu$ of photoexcitation of charge-transfer complexes by electrophilic σ^+ constants[5–7, 13, 14]; and by the fact that nucleophilic reactions of electrogenerated species, even issued from Ph_2Se or Ph_2Se_2, occur namely on this centre[8–10, 18–20] or on aliphatic α-carbon[9, 12, 21].